

Sources, Fate and Transport of Perfluorocarboxylates

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This review describes the sources, fate, and transport of perfluorocarboxylates (PFCAs) in the environment, with a specific focus on perfluorooctanoate (PFO). The global historical industry-wide emissions of total PFCAs from direct (manufacture, use, consumer products) and indirect (PFCA impurities and/or precursors) sources were estimated to be 3200–7300 tonnes. It was estimated that the majority (~80%) of PFCAs have been released to the environment from fluoropolymer manufacture and use. Although indirect sources were estimated to be much less important than direct sources, there were larger uncertainties associated with the calculations for indirect sources. The physical–chemical properties of PFO (negligible vapor pressure, high solubility in water, and moderate sorption to solids) suggested that PFO would accumulate in surface waters. Estimated mass inventories of PFO in various environmental compartments confirmed that surface waters, especially oceans, contain the majority of PFO. The only environmental sinks for PFO were identified to be sediment burial and transport to the deep oceans, implying a long environmental residence time. Transport pathways for PFCAs in the environment were reviewed, and it was concluded that, in addition to atmospheric transport/degradation of precursors, atmospheric and ocean water transport of the PFCAs themselves could significantly contribute to their long-range transport. It was estimated that 2–12 tonnes/year of PFO are transported to the Arctic by oceanic transport, which is greater than the amount estimated to result from atmospheric transport/degradation of precursors.

Introduction

Production of perfluoroalkyl carboxylates [$\text{F}(\text{CF}_2)_n\text{CO}_2$, $n \geq 7$; PFCAs] began in 1947 using an electrochemical fluorination process (1). Early uses documented in 1966 for this “new class of compounds” were based upon their chemical stability, surface tension lowering properties, and ability to create stable foams, and included metal plating and cleaning, coating formulations, fire-fighting foams, polyurethane production, inks, varnishes, vinyl polymerization, lubricants, gasoline, and oil, and water repellents for leather, paper, and textiles (2). Many of these uses were still in practice in the 1990s (3).

PFCAs and their potential precursors are of increasing scientific and regulatory (4) interest because they have been

found globally in wildlife and in humans (5–15). However, the sources of PFCAs in the environment, their physical–chemical properties, and fate and transport are not well understood or described.

This paper provides the first detailed accounting of the direct and indirect sources of PFCAs released into the environment. Typical PFCA compositions are described and historical global emissions from production and use as well as PFCA emissions from potential degradation of poly- and perfluorinated precursors are estimated for the period 1951–2004. Recent industry actions to reduce PFCA global emissions are described. The paper additionally reviews the physical–chemical properties, fate, and transport of PFO for which there is the most available information as representative of PFCAs in general. PFO mass inventories in different environmental compartments are estimated to provide an indication of environmental distribution. Finally, key PFO environmental sinks and transport pathways are scrutinized.

Sources of PFCAs

There are both direct and indirect sources of PFCA emissions to the environment (Figure 1). Direct sources result from the manufacture and use of PFCAs, while indirect sources in the environment are those where PFCAs are present as chemical reaction impurities or where substances may degrade to form PFCAs. The historical period of use or production and an estimation of the global industry-wide emissions for each PFCA “source” are shown in Table 1. The historical emission estimations are provided as ranges based on available data to account for the uncertainty in production, use, and emissions values over time. Computational details for the ranges reported and a summary of chemical substances, their acronyms, and chemical structures are provided in the Supporting Information.

Direct Sources of PFCAs. PFCA Manufacture. PFCAs have been manufactured as salts by four distinct synthesis routes, namely: electrochemical fluorination (ECF), fluorotelomer iodide oxidation, fluorotelomer olefin oxidation, and fluorotelomer iodide carboxylation. Historically, commercial PFCA products were mixtures containing linear eight- or nine-carbon PFCAs as their major component. Depending upon the synthesis route and raw material, the PFCA products also contained homologues ranging from four to thirteen carbons with as much as 30 wt % branched PFCAs present (16, 17). An overview of the chain length composition, predominance of even (E) or odd (O) and straight (S) or branched (B) character from PFCA manufacture is shown in Figure 2. Direct PFCA sources are highlighted in the upper part of Figure 2. The chemical synthesis routes and composition of some representative commercial PFCA products are provided in the Supporting Information.

From 1947 through 2002, the ECF process (16) was used worldwide to manufacture the majority (80–90% in 2000) of

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Direct Sources

Indirect Sources

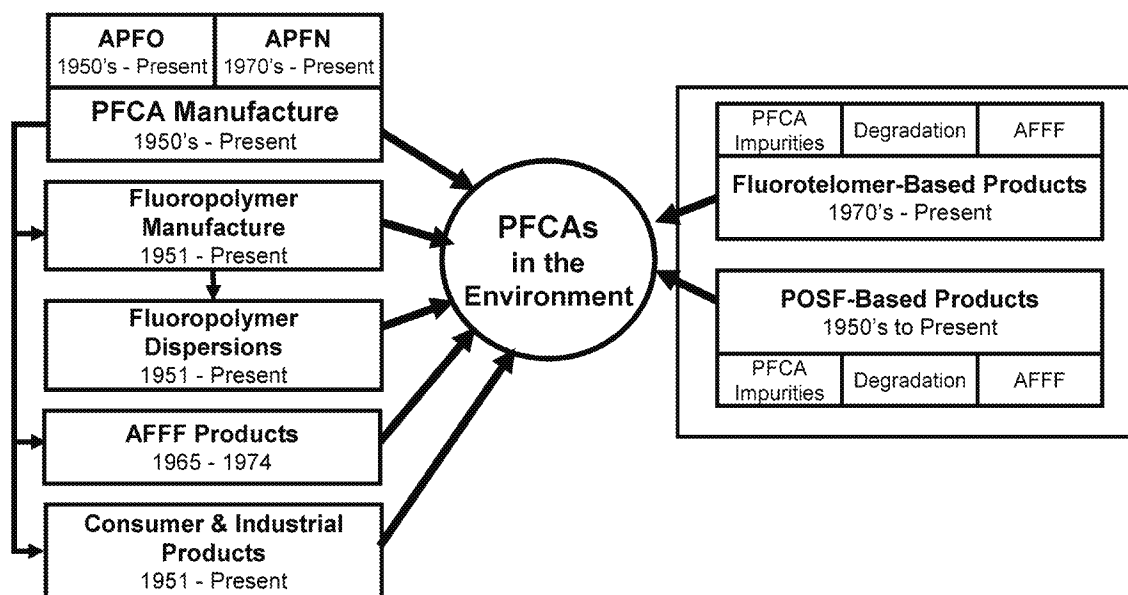


FIGURE 1. Potential sources of perfluorocarboxylates (PFCAs) $\text{F}(\text{CF}_2)_n\text{COO}^-$: APFO = ammonium perfluorooctanoate; APFN = ammonium perfluorononanoate; AFFF = aqueous fire-fighting foam; POSF = perfluorooctylsulfonfyl fluoride.

TABLE 1. Global Historical PFCA Production and Emissions Summary^a

| environmental input source | historical time period (years) | estimated total global historical PFCA emissions (t) | estimated total global production (t) |
|---|--------------------------------|--|---------------------------------------|
| Direct PFCA Sources | | | |
| PFCA manufacture | | | |
| PFO/APFO | 1951–2004 | 400–700 | 3600–5700 |
| PFN/APFN | 1975–2004 | 70–200 | 800–2300 |
| total manufactured | | 470–900 | 4400–8000 |
| Industrial and Consumer Uses | | | |
| fluoropolymer manufacture (APFO) | 1951–2004 | 2000–4000 | |
| fluoropolymer dispersion processing (APFO) | 1951–2004 | 200–300 | |
| fluoropolymer manufacture (APFN) | 1975–2004 | 400–1400 | |
| fluoropolymer processing (APFN) | 1975–2004 | 10–20 | |
| aqueous fire fighting foams (AFFF) | 1965–1974 | 50–100 | |
| consumer and industrial products | 1960–2000 | 40–200 | |
| total direct | | 3200–6900 | |
| Indirect PFCA Sources | | | |
| POSF-based products | | | |
| PFCA residual impurities | 1960–2002 | 20–130 | |
| POSF-based precursor degradation | 1960–2002 | 1–30 | |
| POSF-based AFFF | 1970–2002 | 3–30 | |
| fluorotelomer-based products | | | |
| PFCA residual impurities | 1974–2004 | 0.3–30 | |
| fluorotelomer-based precursor degradation | 1974–2004 | 6–130 | |
| fluorotelomer-based AFFF | 1975–2004 | < 1 | |
| total indirect | | 30–350 | |
| total source emissions (direct + indirect) | | 3200–7300 | |

^a Low and high estimated values as well as the period of use/production for each source are based upon publicly available information cited in the text. See the Supporting Information for additional details.

ammonium perfluorooctanoate (APFO). The largest production sites were in the United States and Belgium, the next largest were in Italy, and small scale producers were located in Japan. The remaining 10–20% of APFO was manufactured from about 1975 to present by direct oxidation of perfluorooctyl iodide (18) at one site in Germany and at least one site in Japan. Solid APFO was used in making fluoropolymers (e.g., Fluorad FC-143) (19). An aqueous solution (e.g., Fluorad FC-118) has been used in recent years because solid APFO

readily sublimates and proved difficult to handle. Additional production, use, and disposal of limited research quantities of PFCAs has taken place in numerous academic and industrial locations worldwide over the past 50 years as indicated by patents and papers in the scientific literature. In 1999, global annual APFO production was approximately 260 tonnes (t) (20). PFO emissions from the largest ECF production plant, located in the United States, were reported to be approximately 20 t (5–10% of total annual production)

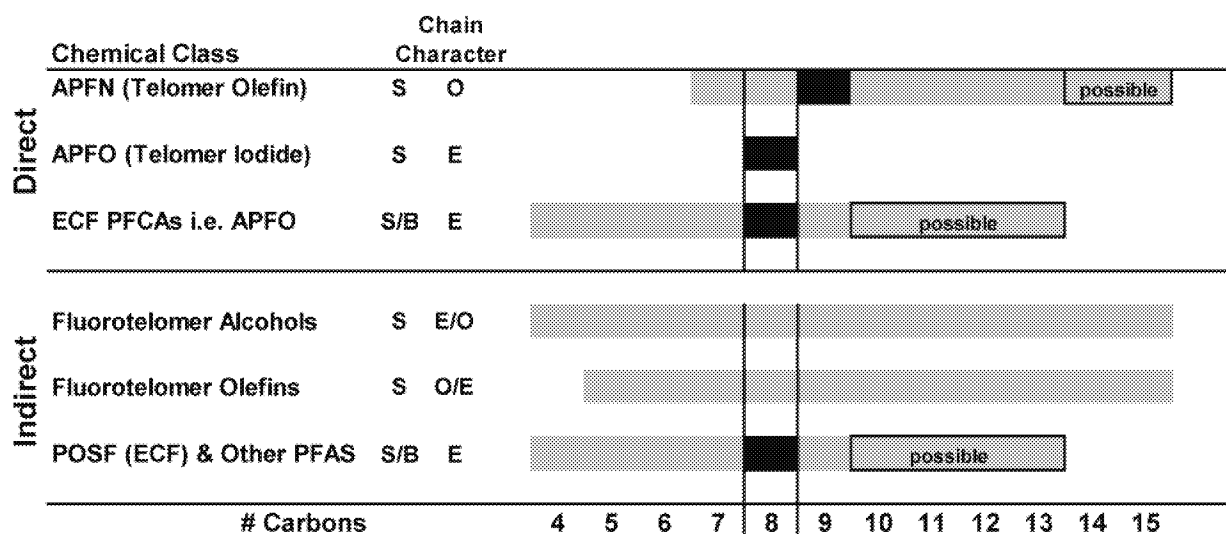


FIGURE 2. Commercial PFCAs composition and chain length distribution: S = contains straight, linear carbon chains; B = contains branched carbon chains; E = even carbon chain(s) predominates; O = odd carbon chain(s) predominate; the black shaded areas highlight the major carbon chain length isomer(s). Shaded areas are the minor carbon chain length isomers. Where noted "possible," it is not clear from information available to what extent these chain lengths have been manufactured. Future producer and monitoring information may provide confirmation.

in 2000, roughly 5% discharged to air and 95% to water (21). The estimated historical (1951–2004) industry-wide global emissions from APFO manufacture are between 400 and 700 t.

By 2002, the principal worldwide APFO manufacturer by the ECF process discontinued external sales and ceased production leaving only a number of relatively small producers in Europe and in Asia (22). New APFO production capacity based on >99% pure perfluorooctyl iodide commenced in the United States in late 2002 with reported annual releases of approximately 50 kg per year to air (23). With the termination of U.S. ECF-based manufacture, current and future U.S. releases from APFO manufacture have been dramatically reduced from many t per year to kg per year. As a result, global APFO manufacturing emissions have decreased from about 45 t in 1999 to about 15 t in 2004 and to an expected 7 t in 2006 (20).

Ammonium perfluorononanoate (APFN) is manufactured primarily in Japan by oxidation of a mixture of linear fluorotelomer olefins (FTOs) to the corresponding odd-numbered PFCAs (24, 25). The principal raw material is 8-2 fluorotelomer olefin (8-2 FTO). Surflon S-111, a commercial product (CAS 72968-3-88), is described as "Fatty acids, C7–13, perfluoro, ammonium salts" a mixture of PFCAs between seven and thirteen carbons in length (26). Patent citations also indicate fluorotelomer iodide carboxylation as a process for APFN production (27). The starting fluorotelomer olefin or iodide dictates the resulting PFCA composition. APFN production is believed to have started in about 1975 (24) and continues today. APFN is primarily used as a processing aid in fluoropolymer manufacture, most notably polyvinylidene fluoride (PVDF). We estimate annual APFN production in 2004 to be between 15 and 75 t. We further estimate emissions to air and water from APFN production to be 10% of the amount produced. Based upon APFN production from 1975 to 2004, estimated historical global emissions from APFN manufacture are between 70 and 200 t. No information was found describing efforts to reduce emissions from APFN manufacture.

Fluoropolymer Manufacture and Processing. PFCAs have been used for over fifty years as processing aids in the manufacture of fluoropolymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) (28). Fluoropolymer manufacture is the single largest direct use

of the ammonium salts of perfluorooctanoic and perfluorononanoic acid (PFOA and PFNA). They act to solubilize fluoromonomers to facilitate their aqueous polymerization.

In 2002, there were 33 fluoropolymer manufacturing sites worldwide located in North America (eight), Japan (seven), China (seven), Europe (seven), Russia (two), and India (one) with a total fluoropolymer manufacturing capacity of 144 000 t (29). The disposition of APFO in 1999 used in fluoropolymer manufacture was 61% emitted, 14% reprocessed, 7% destroyed, and 16% remaining in fluoropolymer dispersion products (20, 31). In 2000, it is estimated that 230–375 t of PFCAs were produced and used globally as processing aids for fluoropolymer manufacture: 85% APFO and 15% APFN. PFCA point source emissions from fluoropolymer manufacturing have been reported to be approximately 60% of the total PFCAs used corresponding to 110 and 250 t per year with 23%, 65%, and 12% distributed to air, water, and land, respectively (20, 31). Reported annual APFO emissions from a European fluoropolymer production plant to air and water were 30 and 4 t, respectively (30). Historical APFO use, emissions, and routes to the environment from 1951 to 2003 for a U.S. fluoropolymer manufacturing site have been recently tabulated (31). Based upon annual industry-wide fluoropolymer production data from 1951 to 2003 (29, 31), estimated historical global PFCA emissions (as APFO and APFN described above) from fluoropolymer manufacture are in the range of 2400–5400 t. Historical use of PFCAs in fluoropolymer manufacturing facilities is the single largest known source of PFCA emissions.

Fluoropolymer manufacturers have recently installed additional capability to capture and recycle APFO (20). Aqueous APFO solutions have been processed for reuse in all regions. Dramatic (>90%) reductions in overall APFO environmental releases over the past few years have been reported (23, 30). The recent historical trend in APFO emissions from fluoropolymer manufacture shows a decrease from hundreds of t in 1999 to less than 50 t projected in 2006. Fluoropolymer producers who use APFN have forecasted a 67% reduction in emissions by 2006 (26).

Fluoropolymer Dispersions. PTFE-based fluoropolymers are manufactured in many ways and processed with different heat histories that dictate APFO disposition (32, 33). Most fluoropolymers are sold as solid granules or pellets with the majority (>99%) of APFO removed (33). Approximately 16%

are sold as aqueous dispersions, which still contain APFO. Dispersion products, made since 1951, typically contain 2000 ppm or less APFO but may contain up to 7000 ppm (34). Customers, called "dispersion processors," generally use the fluoropolymer dispersions to coat metal and fabric surfaces. The coated goods are then subjected to various levels of heat treatment up to and including temperatures which decompose all APFO present (33). Recently, the fluoropolymer manufacturers have completed a study to determine the disposition of APFO during dispersion processing and found that on-average 62% was thermally destroyed and 38% was emitted to the environment (34).

On the basis of total APFO use in fluoropolymer manufacture from 1951 to 2004, estimated total historical global APFO emissions from fluoropolymer dispersion processing are between 200 and 300 t. The Fluoropolymer Manufacturing Group (FMG) recently announced they would reduce the concentration of APFO in fluoropolymer dispersions by at least 90% and thereby dramatically reduce the future emissions from dispersion processing (34). This action will reduce APFO emissions of 20 t in 1999 by 90% in 2006.

PVDF polymers produced using APFN are not generally sold as aqueous dispersions. PVDF polymers are sold as a solid with an estimated residual content of 100–200 ppm APFN. Total global historic APFN emissions from processing of PVDF containing these levels of APFN is estimated to be between 10 and 20 t.

Aqueous Fire-Fighting Foams (AFFF). PFCAs manufactured by the ECF process were used as a component in aqueous fire-fighting foam (AFFF) from approximately 1965 to 1975 (2, 35, 36). In this time period, ECF-based PFCA surfactants in AFFF formulations were used by the military (e.g., at aircraft bases and aboard ship) and in oil and gas production, refining industries, and airports worldwide. Regular training exercises utilizing AFFF formulations containing PFCAs were conducted with direct release to soil and water resulting in widespread input to the environment from a host of point sources located in urban, rural, and remote regions (e.g., the Alaska pipeline after 1977, Northern Region Arctic Military Bases) as well as to the oceans from shipboard and oil rig training exercises (37–41). Annual use of PFCA-based AFFF products is estimated to have been between 5 and 10 t per year from 1965 to 1974. Estimated total historical global PFCA emissions to soil and water from the use of AFFF products based on PFCAs is between 50 and 100 t.

Consumer and Industrial Products. Widespread use of PFCAs and derivatives as additives in industrial and consumer products in 1966 included metal cleaners, electrolytic plating baths, self-shine floor polishes, cement, fire-fighting formulations, varnishes, emulsion polymerization, lubricants, gasoline, and paper, leather, and textile treatments (2). Additional PFCA industrial uses indicated by recent patents and technical bulletins include copier, toner, magnetic recording media, electronic, and semiconductor applications (42–44). The typical concentrations of PFCAs used in industrial formulations range between 100 and 5000 ppm.

PFCAs are indicated in patents as components in consumer products including floor polishes, cleaning formulations, hair care products, inks, medical inhalers, fuel additives, paper, air fresheners, and textile treatments (19, 45–54). Confirmation of these uses, PFCA amounts, and time frame of use have not been determined. It is not known to what extent these patents were actually practiced. It is estimated that annual PFCA use in consumer and industrial products was between 1 and 6 t per year from 1960 to 2000 yielding historical global emissions between 40 and 200 t, most likely to air and water. These industrial and consumer uses represent direct human exposure routes not normally considered.

Indirect Sources of PFCAs. Perfluorooctyl sulfonyl-based (POSF) products made by the ECF process contained PFCA impurities (55–58). Further, fluorotelomer-based products may contain trace levels of PFCAs (<1–100 ppm) as unintended reaction byproducts (59). Investigations to determine the environmental fate through the life cycle (manufacture, use, and disposal) of these two different material classes have revealed that there are potential transformation pathways by which some raw materials from each class may degrade to form PFCAs in the environment (60–65).

POSF-Based Products. POSF-based products have been manufactured at several sites in the United States as well as sites in Belgium, Italy, Germany, and Japan. Production began in the 1960s and increased until the principal (estimated 80–90% market share) manufacturer phased out production in 2002 (58). Global production by the major manufacturer of POSF as a raw material in 2000 was approximately 3700 t (58). The global use, distribution, and release of POSF-based products have been reported (66). Uses included industrial applications and consumer products (i.e., food-contact paper, spray cans for do-it-yourself-application) worldwide.

POSF-based products contained between 200 and 1600 ppm of PFO (56). Although principally composed of eight-carbon fluorinated chains, the PFCA impurities in POSF-based product were a mixture of linear and branched (up to 30 wt %) chain isomers from four to nine carbons in length (17). A recent analysis of a series of consumer spray application products revealed PFCAs from six to nine carbons ranging in concentration from 5 to 100 ppm (67). Perfluorodecyl- and perfluorododecyl-sulfonates have recently been reported in environmental samples (68, 69). Their origin has not been determined. However, if these sulfonates originate from ECF processes, PFCAs, both linear and branched, of the same chain lengths would also be expected to be present in the environment. The PFCAs present in POSF-based products were emitted to the environment (principally air and water) from point sources as well as dispersive use and disposal (i.e., landfill and incineration) of industrial and consumer products (i.e., textile fabrics, carpet, and paper). On the basis of the reported data for global production of POSF-based products (58) and a use period from 1960 to 2002, the global historical emissions of PFCAs from POSF products are estimated to be between 20 and 130 t.

POSF-based products replaced PFCAs as AFFF surfactants and became the products of choice for fire protection companies and suppliers from the 1970s forward. These products contained between 0.1 and 1.0 wt % of PFCAs with PFO as the largest component (37–39). Although no longer manufactured, POSF-based AFFF products are still in use today from inventories previously in place (70, 71). As noted earlier, AFFF use resulted in widespread input to water and soil from sources in urban, rural, and remote regions, including the Arctic, as well as to the oceans from shipboard and oil rig training exercises. Based upon historical emission of PFCAs from 1970 to 2004, total global emissions of PFCAs are estimated to be between 3 and 30 t from this source.

Degradation of POSF-based residual raw materials and products is also a potential indirect source of PFCAs in the environment. However, there is little information regarding their degradation pathways and more studies are needed. It has been reported that 0.6% of raw material sulfonamide alcohol N-EtFOSE, $F(CF_2)_8SO_2N(Et)CH_2CH_2OH$, was transformed to perfluorooctanoate in a biodegradation study (64). N-EtFOSE and N-MeFOSE have been reported to be present in outdoor and indoor air (72). The atmospheric degradation of perfluoroalkylsulfonamido raw materials to PFCAs has recently been reported (73, 74). Utilizing the POSF historical production, residual POSF-based raw materials between 0.1

and 3.0 wt %, and 0.5–1.0% degradation of these raw materials to PFCAs, estimated total historical global emissions of PFCAs from 1960 to 2002 from degradation of POSF-based raw materials are between 1 and 30 t.

To date, there is no scientific evidence that POSF-based polymeric or surfactant products degrade to form PFCAs under environmentally relevant conditions. These products have been released into the environment (e.g., landfills, wastewater sludge) and have also been subject to incineration and recycling (66). As such, they may represent a latent source of PFCAs if they degrade in these situations. A recent incineration study showed that only one- and two-carbon fluorinated species arise from thermal degradation of POSF-based substances (75).

Numerous POSF derivatives, most notably PFOS, have been found widely in people and the environment (5–15). If the PFCAs present in POSF-based products followed the same exposure and environmental release pathways, they would be expected to be present in people and the environment as well. A “signature” of PFCAs originating from ECF manufacture would be the presence of branched PFCA isomers. Additional research is needed to fully determine the significance of these potential exposure and release pathways and whether PFCA isomers have similar or different environmental and biological partitioning behavior, fate, and transport.

Fluorotelomer-Based Products. Fluorotelomer-based products have been manufactured since the early 1970s and used in many of the same industrial and consumer product applications as POSF-based products (17, 76). Telomer A is the basic raw material manufactured at one site in the United States, one site in Germany, and two sites in Japan. It is likely that other smaller manufacturing and processing facilities exist as well. Fluorotelomer-based raw materials and products are manufactured by a series of steps beginning with Telomer A (see Supporting Information). Global Telomer A production between 2000 and 2002 was between 5000 and 6000 t per year (77). Subsequent chemical reactions create fluorotelomer raw materials such as fluorotelomer iodides, olefins, alcohols, and acrylate monomer.

Two methods are used to manufacture fluorotelomer alcohol (FTOH) from fluorotelomer iodide: sulfation/hydrolysis and solvolysis (76). In both, 2% or less residual unreacted fluorotelomer iodide remains. Additionally, 2–5 wt % byproduct fluorotelomer olefin (FTO) is formed in the solvolysis process. Similarly, fluorotelomer alcohol or fluorotelomer iodide is used to make acrylate monomer, a fundamental building block for the polymeric products representing >80% of the fluorotelomer-based products manufactured and used worldwide. The reaction of fluorotelomer alcohol to make fluorotelomer acrylate or methacrylate esters leaves 0.1–0.5 wt % unreacted residual FTOH. Alternatively, reaction of fluorotelomer iodide and acrylic acid salt to form acrylate monomer results in 3–8 wt % FTO byproduct (78). The FTOHs and FTOs are present in the ultimate sales products unless removed. Using the 5000–6000 t of Telomer A production in 2002, it is estimated that 2 wt %, or approximately 100 t, each of FTOHs and FTOs were present annually in fluorotelomer-based products.

Residual fluorotelomer raw materials are potential indirect sources of PFCAs. They may react during chemical processing and form PFCAs (e.g., Telomer A oxidation) (18). Trace levels of PFCAs, including PFO, may be present in some fluorotelomer-based products as unintended manufacturing byproducts (<1–100 ppm) (59). Environmental release of PFO to air and water from a fluorotelomer-based products manufacturing facility as a point source was reported to be less than 1 kg to air and less than 100 kg to water per year (79). Recent study results show that trace levels of PFO or fluorotelomer alcohols (FTOHs) present in fluorotelomer-

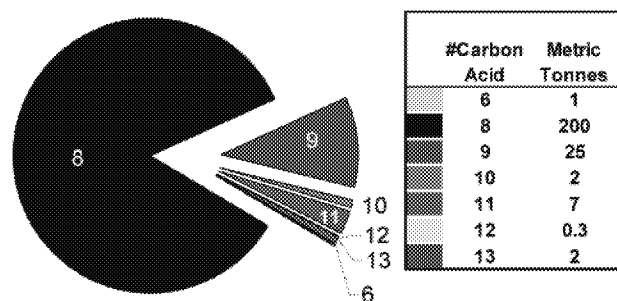
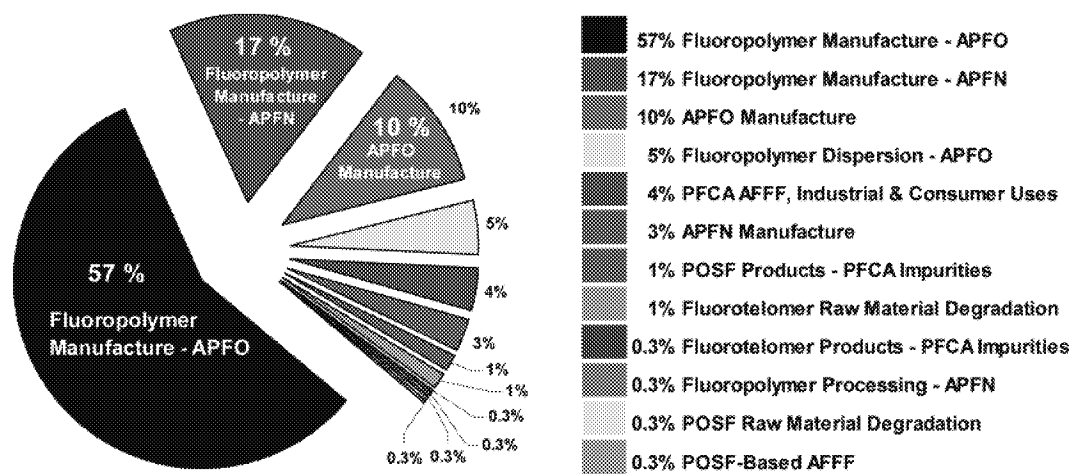
based products are likely to be released to the air during industrial application of fluorotelomer-based products to textiles (80). Estimated historical global emissions from 1974 to 2004 of PFCAs to air and/or water from fluorotelomer-based products containing 1–100 ppm trace levels of PFCAs are between 0.3 and 30 t.

Environmental degradation of fluorotelomer raw materials present in fluorotelomer-based products is a potential indirect source of PFCAs. It is estimated that from 2000 to 2002, fluorotelomer-based products contained a sum total of approximately 200 t per year of FTOH residual raw material and FTO as a reaction byproduct. FTOHs and FTOs have sufficient vapor pressure to be present in air (81). FTOHs with 6, 8, and 10 fluorinated carbons have been identified in air samples (82, 83). The 100 t of FTOHs residual in the total global manufacture of fluorotelomer products from 2000 to 2002 is at the low end of the computed 100–1000 t/year global input necessary to maintain reported atmospheric FTOH concentrations (84). No atmospheric monitoring data has been reported for FTOs. It has been reported that 1–10% of FTOHs present in air in the gas phase may transform to PFCAs by reaction with HO_x in atmospheric conditions where NO_x is absent. No PFCAs are predicted to form when NO_x is present in concentrations common in urban and boreal regions (63). FTOs are likely to degrade by reaction with HO_x in the atmosphere by the same transformation pathway as FTOHs (85). An additional atmospheric pathway which may be important for FTOs is reaction with ozone. Ozonolysis of FTOs directly produces odd-numbered PFCAs. Substantial data gaps must be explored to elucidate the atmospheric partitioning and fate (e.g., photolysis, partitioning, sorption) of FTOHs and FTOs in order to fully describe the atmospheric fate of these substances.

Studies to determine the biodegradation in sludge of fluorotelomer alcohols have reported 3–6 wt % formation of PFO (60–62). Assuming 1.0–2.0 wt % FTOH and/or FTO present per unit Telomer A produced and 1–10% degradation to PFCAs, the global historical contribution from 1974 to 2004 of PFCAs due to degradation of FTOHs and FTOs is estimated to be between 6 and 130 t. One telomer manufacturer recently announced their intent to implement process technology that will significantly reduce residual fluorotelomer raw materials and PFCAs in products (23).

Finally, degradation of fluorotelomer-based polymeric products represents a potential indirect source of PFCAs from degradation during use (e.g., sewage treatment plant sludge from laundering textiles) or disposal (e.g., landfill or incineration). Recent studies showed that no PFO was formed under simulated typical municipal incineration conditions of fabrics treated with fluorotelomer-based polymers (86). Twenty-eight day degradation studies in sludge and soil did not indicate polymer degradation to PFO (87, 88). Long-term (up to one year) abiotic and biotic degradation studies of fluorotelomer-based polymeric products in soils, sediments, and anaerobic sludge are underway (89). To date, there is no scientific evidence that fluorotelomer-based polymers degrade to form PFCAs under environmentally relevant and representative conditions.

The predominant AFFF agents produced and sold globally until May 2000 were POSF-based surfactant products (40, 70, 71). Fluorotelomer-based AFFF surfactant products became available in the 1970s. Because the POSF-based products were well established and specified in long-term government contracts, fluorotelomer-based AFFF products had a market share of less than 50% for most of the 30 years both were in use until POSF-based products manufacture ceased. Fluorotelomer-based AFFF surfactants are principally C₆F₁₃-chains with small amounts of longer perfluorocarbon chains (37). The primary conclusion from recent monitoring studies was that PFCAs present in the groundwater from fire



training exercises and actual use originated from the POSF-based products and not from fluorotelomer-based products (37). The primary degradation product of the fluorotelomer-based AFFF agents was reported to be the 6-2 fluorotelomer sulfonate ($(C_6F_{13}CH_2CH_2SO_3^-)$).

Summary. PFCA Sources. Total industry-wide global historical PFCA emissions to the environment are dominated by releases from fluoropolymer manufacture and comprised mainly of 8-, 9-, and 11-carbon PFCAs. Figure 3 shows the global historical emissions for each potential PFCA source using the midpoint of the range in Table 1. Figure 4 presents a view of estimated PFCA emissions in the year 2000 by chain length. A figure showing the sum of direct and indirect PFO sources from 1999 to 2006 (projected) is included in the Supporting Information. A 60% reduction in APFO emissions has occurred between 1999 and 2004. The reduction is projected to be >75% by 2006. These emission data provide a basis for exploring the global fate and transport of PFO, which is the focus of the remainder of the paper.

Physical—Chemical Properties

This section summarizes the physical–chemical properties of PFO and PFOA and uses them to provide an indication of their environmental behavior.

The low reported pK_a values of PFOA of 2–3 (17, 90) indicate that both PFO and PFOA are present in the environment. PFO and PFOA have different physical–chemical properties and environmental partitioning behavior. At pH 7, only 3–6 in 100 000 molecules are PFOA, with the remaining being PFO. At pH 4, about 6% will be PFOA molecules.

The vapor pressure (V_P) for PFO has not been measured but is expected to be negligible. Vapor pressures of PFOA and perfluorononanoic, -decanoic, -undecanoic, and -dodecanoic acids have been measured at the temperature range 59.25–190.80 °C (97). Vapor pressures were shown to decrease

with increasing chain length of the acid. Extrapolation of the Antoine equation to 25 °C for PFOA results in an estimated V_p of 4.2 Pa. In the same study, solid APFO was shown to readily sublime to gaseous PFOA at room temperatures.

The solubility of PFO in water is reported to be 4.1 g/L at 22 °C (92) and 9.5 g/L at 25 °C (93). The sharp increase of solubility with temperature is qualitatively consistent with the reported Krafft point of PFO of 20 °C and critical micelle concentration (CMC) of 3.7 g/L (94). The Krafft temperature is the limit at which compounds cease to be singly dispersed and begin to form micelles. Above the Krafft point, the solubility increases abruptly on account of the formation of micelles. The solubility of PFOA in water has not been published, although it is expected to be less soluble than PFO. The aqueous solubility of PFOA could be determined in a concentrated acid solution.

PFO/PFOA is expected to form multiple layers in octanol/water making determination of the octanol–water partition coefficient (K_{OW}) extremely difficult (90). K_{OW} may anyway be an irrelevant measurement for estimating the environmental partitioning of perfluorinated compounds (95, 96).

No measurements of the Henry's law constant (H) have been made for PFO or PFOA. H is usually given by the ratio of vapor pressure and water solubility (97). Care should be taken in calculating H for PFOA and PFO. It is critical that water solubility and vapor pressure measurements are for the same species. H for PFO is expected to be very low and H for PFOA is expected to be relatively high so that any volatilization that occurs is likely to be of PFOA. However, the volatilization of PFOA from water will depend on the environmental pH. The proportion of PFOA is approximately 15 000–30 000 times lower than PFO at pH 7 making volatilization from water unlikely. Under acid conditions (e.g., pH 4), 6% would be PFOA, thus a larger fraction would be available to volatilize.

The sorption mechanism of PFO to solids is not well characterized. Soil-water partition coefficients for six PFCAs in six soil types of 2–40% organic carbon (OC) content have been determined (98). Soil-water partition coefficient (K_d) values of PFCAs exhibited linear relationships with soil OC content and K_{OC} increased with chain length of the acid. A K_{OC} of 52 L/kg was reported for PFO. A recent industry study (99) in which the sorption/desorption behavior of APFO was tested for four different soil types (0.8–5.8% OC) confirmed these results. K_d s for the soils were again linearly correlated with OC content with K_{OC} s varying between 49 and 230 L/kg. Sorption isotherms were linear over a wide concentration range. A strong inverse relationship between OC content and desorption was also shown. Finally, a separate study reported a lower K_{OC} for PFO in soil of 17 L/kg (100). It is

likely that sediment–water partitioning exhibits behavior similar to soil–water partitioning.

Bioconcentration factor (BCF) measurements with rainbow trout for a suite of PFCAs (8–12 carbons) yielded BCFs from 4.0 (PFO) to 23 000 (101), indicating that BCF increases with carbon chain length (a factor of 8 for each additional carbon). It is noteworthy that there was a strong correlation between hydrophobicity, as indicated by CMC (17, 102), and measured BCFs (101) and K_{OC} s (98). Bioconcentration and sorption models based on CMC (102) that have been previously developed for other surfactants may also be applicable to the PFCAs.

If present in the atmosphere, PFO is expected to be associated with particles since its vapor pressure is thought to be negligible. PFO could either bind to the organic phase in aerosols and/or dissolve in water present in the aerosols. PFOA is volatile and may be present in the air. Measurement of PFOA/PFO in the gas and aerosol phases in air is recommended.

In summary, PFOA is expected to dissociate in the environment almost entirely to PFO. PFO has negligible vapor pressure, a high solubility in water, and moderate sorption to solids. Based on these properties, accumulation in surface waters is expected. Limited environmentally relevant physical–chemical properties and partitioning data prohibit the application of classical fate models based on partitioning in the air/water/octanol system (97).

Environmental Inventories and Sinks

Environmental Inventories. In this section, environmental monitoring data are reviewed and used to estimate mass inventories in different environmental compartments, and the key sinks are considered. In making inventory estimations it is necessary to estimate the regional background concentrations in an environmental compartment and then multiply the concentration by the volume or mass of the compartment. Samples taken near obvious point sources are thus excluded to avoid positive bias in the inventory estimations. A major limitation in the inventory estimates is the lack of literature studies reporting environmental levels. To account for the wide variability in environmental concentrations and physical processes, all calculations provide a minimum and maximum estimated PFO environmental inventory range. The inventory calculations are only undertaken for the northern hemisphere environment because monitoring data for the southern hemisphere are absent. Inventories in the southern hemisphere are expected to be much lower because no significant production or use of PFCAs is known to have occurred there and atmospheric and aquatic mass exchange between the two hemispheres is generally limited (103).

Ocean Water. Coastal water samples have been taken near densely populated or industrialized countries/regions (e.g., SE Asia and North Sea) (104–109) and in the Faroe Islands (110). Major riverine and sewage treatment input would be significant for most of these sites. Reported PFO levels in coastal waters generally vary between 0.2 and 20 ng/L, but were as high as 450 ng/L in SE Asia samples.

PFOA concentrations in open ocean samples, both surface and as deep as 4400 m, have been reported for a number of seas and oceans (106–109). PFO levels were orders of magnitude lower than in coastal areas with concentrations in surface open ocean waters varying from 0.015 (Central to Eastern Pacific Ocean) (107) to 0.5 ng/L (open North Sea) (108).

A deep ocean water PFO concentration of 69 pg/L (1000–4400 m) has been reported (107). Surface levels in the same area were 107 pg/L. Since PFO has been manufactured for about 50 years and mixing of water between the surface layer and deep ocean is very slow (deep ocean water has a residence

time of several hundred years) (111), these deep ocean concentrations are difficult to explain and need to be confirmed.

For the ocean inventory calculations, a northern hemisphere ocean surface area ($1.5 \times 10^{14} \text{ m}^2$) was extracted from a global model (112) and the sea surface mixed layer was assumed to vary between 50 and 150 m. PFO was assumed well-mixed throughout the surface mixed layer. Open ocean water concentrations used for calculations were taken from the Eastern Pacific (0.015–0.142 ng/L) and North Atlantic (0.100–0.439 ng/L) (107), as these two oceans comprise the greatest surface area in the northern hemisphere. The range of open ocean concentrations used in the calculations was thus 0.015–0.439 ng/L. The total estimated PFO inventory in ocean waters is between 110 and 10 000 t. The broad range reflects both the high scatter in measured PFO levels and the variance in the assumed depth of the surface mixed layer.

Freshwater. There are several studies reporting freshwater concentrations (104, 106, 108, 110, 113–116). The most comprehensive survey of freshwaters was undertaken in Japan (104) in which most major Japanese rivers and several lakes were sampled. This survey showed that PFO concentrations in Japanese surface waters could be as low as 0.1 ng/L in remote areas and about 2–10 ng/L in urban areas. There were some sites where much higher levels of PFO were reported, but these were shown to be near point sources. Recent studies in the Great Lakes report water concentrations of PFO in the same range as the Japanese study of 2–40 ng/L (113, 114). The data from ref 114 reporting 40 ng/L of PFO in Lake Ontario have been questioned on the grounds of data quality (117). Furdul et al. (113) claim not to have the same blank problems that were alleged to prejudice data quality in ref 114 and report concentrations of PFO of 2–8 ng/L in several of the Great Lakes. Similar low ng/L levels have been reported in Scandinavia (110) and in the Elbe River (108).

For the calculation of PFO in freshwater, it is assumed that freshwaters can have concentrations between 0.1 (remote areas) and 10 ng/L (high end of concentrations reported in rivers or lakes). Using estimated freshwater surface area for the northern hemisphere of $4 \times 10^{12} \text{ m}^2$ and an assumed average depth of 20 m taken from a global model (112), the inventory is estimated as 4–800 t.

Sediments. Fresh and coastal water sediment concentrations of PFO have been reported (68, 118–121). These studies collected sediments from a small U.S. city (Port St. Lucie, FL), The Netherlands, several Scandinavian countries, San Francisco Bay, and the Niagara River. Reported PFO concentrations in sediments were 24 pg/g to 18 ng/g. Samples with concentrations of over 1 ng/g were atypical (possibly in vicinity of point source) with the majority of reported concentrations being in the hundreds pg/g range. For inventory calculations we assumed a concentration range of 20 pg/g (lowest reported) to 500 pg/g (high end of concentrations reported in rivers, lakes, or coastal zones, away from point sources).

To calculate the sediment inventory, sediment areas were taken from a global model (112) and values for typical sediment particle density (2.4 g/cm^3), bioturbated mixing depth (5 cm), and surface sediment porosity (0.7) were used (97, 112). The estimated PFO sediment inventory is 3–340 t.

Air. PFCAs have not been reported in the vapor or particle phase of background air samples. Kallenborn et al. identified PFO in precipitation from Finnish and Swedish locations with a concentration range of 8–17 ng/L (110). Furthermore, Scott et al. (122) found PFO as high as 50 ng/L (but generally less than 10 ng/L) in precipitation samples from 3 different U.S. sites during 1998. Loewen et al. (123) reported PFOS in rainfall collected in Winnipeg, MB but no PFCAs were

detected. Young et al. (124) reported PFOA levels of about 2–3 ng/L in snow and ice caps in the High Arctic.

The presence of PFO in rainfall and snow indicates the atmospheric presence of PFCAs. This could be the result of point sources in the immediate vicinity of the sampling stations, or the atmospheric transport of PFCAs themselves or volatile precursors which undergo transformation to PFCAs. More research on this topic is highly recommended.

Calculation of the amount of PFO/PFOA in the atmosphere is not currently possible due to lack of data. It is expected, however, that the total mass would be low compared to the masses in surface waters and sediments.

Other Media. Due to lack of data for PFO in background soils, it was not possible to calculate a soil inventory. Soils will receive PFCAs via atmospheric wet deposition (110, 122) and possibly dry deposition, but retention by the soil is expected to be low compared to other well-known hydrophobic organics. Monitoring of PFCAs in background soils is needed to test this hypothesis.

Numerous studies have reported concentrations of PFCAs in biota and humans (5–15). However, it is difficult to use these data to calculate an inventory for biota. It was not attempted, as we do not expect biota to contain a significant mass of PFCAs compared to masses in surface waters and sediments.

Environmental Sinks. Degradation. PFCAs are stable to acids, bases, oxidants, and reductants and are generally not believed to undergo metabolic or other degradation in the environment (17). Historical losses through degradation are assumed to be negligible.

Transport to Deep Ocean Water. PFCAs may be transported to deeper water through the physical, downward movement of water containing them or through sedimentation on sinking particles (125). The residence time of the mixing of the surface mixed layer with the deeper ocean water is between 300 and 500 years (111). The estimated removal rate of PFO from the surface mixed layer to deeper water can be calculated as ocean inventory/residence time, which yields an estimated current annual removal rate of 0.2–33 t/year. It is currently not possible to calculate the sedimentation loss for PFO (although it is expected to be low) because water particulate concentrations in the open ocean are unknown.

Sediment Burial. Sediment burial refers to removal of PFO below the bioturbated mixed layer that is available for exchange with the overlying water column. The burial loss is computed using knowledge of the sediment inventory estimated here, sedimentation rate (0.1–0.3 cm/year) (97), time period (50 years), and bioturbated mixing depth (5 cm, 97) and yields a current annual removal rate of 0.1–21 t/year.

Summary—Inventories and Sinks. The calculations in this section suggest that oceans contain the majority of PFO historically released. This is consistent with our knowledge of the physical–chemical properties of PFO and the fact that a large proportion of emissions are released to surface waters. The only environmental sinks for PFO are considered to be sediment burial and transport to the deep oceans, implying a very long environmental residence time. It is believed that direct comparison of inventories and emissions provides an approximate mass balance since only a small percentage of the PFO historically released is expected to have been removed from the environment. The total environmental release of PFO can be estimated as 85% (see Figure 4) of the total PFCA releases (3200–7300 t) which is 2700–6200 t. It is encouraging to observe that the sum of total environmental inventories (120–11 000 t) is in the same range, but due to large uncertainty boundaries the current mass balance is inconclusive. To provide improved mass balances in the future, more monitoring data are needed to lower the uncertainty boundaries in the inventory estimates and to identify other possible reservoirs for PFO (e.g., soil).

It is worthy of additional note that levels of PFN in the open oceans are about an order of magnitude lower than those of PFO (105–110, 126). Providing that oceans are the major repository of PFCAs, the lower levels of PFN relative to PFO provide support for our estimate that the historical cumulative emissions of APFN/PFNA are an order of magnitude lower than those of APFO/PFOA (Figure 4).

Environmental Transport Pathways

Atmospheric Transport of Volatile Precursors. The degradation and transport of volatile precursor chemicals such as FTOHs have been hypothesized as the main source of long-chain PFCAs in remote regions such as the Arctic (63, 84). Not considered and yet to be investigated are potential precursors such as fluorotelomer olefins (FTOs) and perfluorosulfonyl chemicals and potential local sources. More physical–chemical data for FTOHs as well as information on gas–particle partitioning and atmospheric deposition would improve calculations of atmospheric transport.

Atmospheric Transport of APFO/PFOA. There is evidence that APFO/PFOA is directly released to the atmosphere at fluoropolymer manufacturing facilities (127). Air samples taken at locations surrounding one manufacturing facility revealed on analysis levels of APFO/PFOA in atmospheric particulates. Given the high vapor pressure of PFOA, it seems unlikely that it is present on atmospheric particulates. The compound detected on the particulates may therefore be solid APFO, which is consistent with the use of APFO in the fluoropolymer manufacturing process. No vapor phase PFOA was detected above a detection limit of 0.07 $\mu\text{g}/\text{m}^3$. The lifetime of these particulates in the atmosphere and, thus, their travel distance will depend on the particle size. Less than 6% of particles were $>4\text{ }\mu\text{m}$, while almost 60% of the particles were below $0.3\text{ }\mu\text{m}$. As the vent gases are diluted by ambient air and the APFO particles move away from the source, they may sublime to form gaseous PFOA further increasing travel distances. Gaseous PFOA in the atmosphere can arise from the atmospheric degradation of precursors, from emission of APFO followed by sublimation, and from volatilization (91). The atmospheric lifetimes of gaseous 1–4-carbon PFCAs (128) and PFOA (129) have previously been examined and are thought to be dependent on removal by wet and dry deposition rather than removal by reaction with hydroxyl radicals. Atmospheric lifetimes for gaseous PFOA of a few days to several weeks have been estimated (129). Further studies are required to determine whether direct atmospheric transport of APFO/PFOA is a significant pathway for long-range transport.

Atmospheric Transport of PFO on Marine Aerosols. Marine aerosol (a significant part of atmospheric aerosol) is generated through gas-bubble production and collapse through breaking waves and rough sea conditions (130). The sea surface micro-layer can, thus, supply the atmosphere with organic-rich particles that should be considered as a possible contributor to the long-range transport and widespread global distribution of PFCAs, even in remote regions. This transport pathway is expected to be especially important for surfactants such as PFCAs based on the fact that high concentrations of water-soluble hydrocarbon surfactants have been shown to accumulate on the upper sea layers and sea surface (130–135). Studies are needed to determine whether and to what extent marine aerosols contain PFCAs and may contribute to their global transport.

Aquatic Transport. There is strong evidence for the importance of aquatic transport of hexachlorocyclohexanes to the Arctic (136, 137). These chemicals are semi-volatile, environmentally persistent, and only sparingly water soluble (138). As PFCAs are highly water-soluble and persistent, they are hypothesized to have a high potential for long-range aquatic transport to the Arctic. To explore this hypothesis,

we have used the approach presented in Macdonald et al. (137) to estimate the quantity of PFO that is transported to the Arctic by the oceans. The total flow of water entering the Arctic surface ocean (mainly through West Spitzbergen Current, Barents Sea, Norwegian Current, and Bering Strait) is approximately $(4.86 \pm 1.3) \times 10^6 \text{ m}^3/\text{s}$ (137). By taking the lowest reported open ocean PFO water concentrations of 0.015–0.062 ng/L (central Pacific Ocean) as representative of background levels in the northern hemisphere (107) and multiplying by the water flow rate, the PFO that reaches the Arctic is calculated to be between 2 and 12 t per year. Unpublished data presented recently (139) demonstrated that the Pacific Ocean water concentrations used in this calculation are similar to concentrations of PFO in Arctic waters (Greenland Sea). PFOA and PFOS were present in all samples with concentrations ranging between 0.020 and 0.120 ng/L.

The flow paths of surface ocean currents and time scale for them to be transported to the Arctic Ocean are best known for the North Atlantic based on studies using radionuclide tracers (140–142). For example, it takes 5–7 years for ^{137}Cs to travel from the Irish Sea to the entrance of the Arctic Ocean. Considering that PFCAs have been emitted for approximately 50 years and accumulating in the oceans, ocean water transport to the Arctic is likely to be important. As a point of comparison, between 0.1 and 1 t per year of PFCAs was estimated to be delivered to the Arctic from the northern hemisphere from FTOH degradation and subsequent atmospheric deposition (124, 143). Thus, ocean water transport is estimated to be more significant as an input route to the Arctic. We recommend that the relative importance of these two pathways be further examined. Ocean transport and degradation of precursor chemicals detected in water should also be considered.

A complication in comparing these pathways is that in the environment the pathways will combine. Ocean water transport of PFCAs is the combination of (a) discharges of PFCAs to surface waters and subsequent transport, (b) atmospheric loadings of PFCAs to surface waters and subsequent transport, and (c) discharge of precursors to surface waters, transformation to PFCAs, and subsequent transport. Atmospheric transport of PFCAs is the combination of (a) discharges of PFCAs to the atmosphere and subsequent transport, (b) discharge of precursors, transformation to PFCAs and subsequent transport, and (c) surface-air transport of PFCAs and subsequent atmospheric transport. These processes are likely to occur multiple times as these compounds are transported around the globe, a process sometimes described as “grasshopping” (144).

Source Patterns. Patterns in chain lengths and the branching of PFCAs in environmental samples may provide clues to their sources and transport pathways. Branched PFCAs are only known to arise from the ECF production processes. Likewise, PFCAs with carbon chain lengths greater than or equal to 14 are likely to arise from fluorotelomer-based substances, as a direct source from their use in PFCA manufacture, or as an indirect source from degradation. Associating chain length patterns in environmental samples to patterns in sources is complicated because patterns may become altered as a result of different partitioning and uptake/clearance rates in biota for the various PFCAs. However, it is interesting to note that the PFCA emissions pattern shown in Figure 4, odd-carbon PFCAs 9, 11, and 13 from highest to lowest each being greater than their next-highest even numbered PFCA homologue 10, 12, or 14, originating largely from direct sources, matches the patterns reported in biota sampled from remote regions (9, 14).

Differences have been observed in chain length patterns of PFCAs in polar bear livers in the Eastern and Western Arctic (15); e.g., a higher ratio of PFNA/PFOA in the Western

Arctic than in the Eastern Arctic. If PFCAs are transported via wind and/or ocean currents, then the prevailing pathways suggest that the source of PFCAs in the Eastern Arctic is attributable to transport from Western Europe and Eastern North America, while the Western Arctic would be influenced mainly by Eastern European sources (15). Interestingly, the higher PFNA/PFOA ratio in the Western Arctic is consistent with the manufacture and use of PFNA/APFN in Eastern Asia.

Time Trends in Biota. Studies that report increasing concentrations of some PFCAs with time in Arctic ringed seals, sea birds, and polar bears from the early 1970s to early 2000s (145, 146) have been suggested to provide evidence for the importance of transport/degradation of precursors as a mechanism for delivery of PFCAs to the Arctic. It is recommended that these datasets are statistically analyzed to determine if the upward slopes of concentrations are significant and to determine confidence intervals for the reported doubling times. The age of animals studied should also be taken into account, which is complicated by the contradictory nature of recent literature studies (147, 148). One recent study claims no significant change in the concentrations of PFCAs in polar bear livers with age (147), whereas another suggests a significant increase in liver concentrations with age (148). Nevertheless, all the possible transport pathways discussed in this paper could explain an increasing trend in Arctic levels of PFCAs. Even though ocean water transport is relatively slow compared to atmospheric transport, it could still explain recent rising Arctic levels in aquatic wildlife because direct sources of PFCAs to surface waters have been increasing sharply for several decades since the 1950s.

The apparent downturn in perfluorooctane sulfonate (PFOS) concentrations reported in aquatic wildlife since 2000 (145, 149) is currently under investigation. It seems unclear whether (a) the species studied could clear PFOS so rapidly or (b) concentrations in the exposure media (water and food) of these species would have decreased so rapidly even if atmospheric deposition of PFOS has declined as a result of emission reductions.

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Supporting Information Available

Details of manufacturing schematics for PFCAs and fluorotelomer based products, PFCA weight composition of commercial products, recent and projected emissions of PFO/APFO, and details of all emission, inventory, and sink calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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